

## A METHOD FOR THE CONVERSION OF GYPSUM INTO SODIUM SULPHATE

Mohammad Saeed, Salih Mansoor, A. Khaliq and M.K. Bhatti

*PCSIR Laboratories, Lahore, Pakistan*

(Received February 17, 1983)

Production of sodium sulphate by the action of sodium chloride on indigenous gypsum has been studied. The work describes two methods utilising cation exchange resin whereby 90 % of gypsum has been transformed into sodium sulphate of 90 % purity. In the first method gypsum powder was used and particle size (400 mesh) caused completion of reaction in 7 min whereas 13 and 28 min were required respectively for 300 and 200 mesh size. In the second method same results were achieved without grinding gypsum thus eliminating an energy consuming step. One cubic foot of resin could convert 1 kg of gypsum and 700 g sodium chloride into 900 g of sodium sulphate with 570 g calcium chloride as by product. The final product of 98 % purity was obtained by primary evaporation in a solar tank followed by final evaporation by natural gas.

### INTRODUCTION

An attempt to convert gypsum directly into sodium sulphate by interaction with rock salt was made by Bauers *et al.* [1] who melted an intimate mixture of cryolite salt and gypsum and extracted sodium sulphate by leaching the mass. This process required high temperature and produced impure product. Another study in this respect was reported by Stave *et al.* [2] by reacting the chlorides of sodium and potassium with gypsum in the presence of silica at 800–900°. This method has its limitations due to the decomposition of the product during the process. Joseph N. Murad [3] was able to produce sodium sulphate from gypsum and sodium bicarbonate. A similar process was developed by Silvia *et al.* [4] who used soda ash instead of sodium bicarbonate. Georgeta *et al.* [5] obtained sodium sulphate and magnesium salts from gypsum, dolomite and rock salt by calcination of the reactants. Copper production processes, sodium dichromate and Rayon Manufacturing Industries also yield some quantities of sodium sulphate as a by-product [6–7]. In addition to these methods sodium sulphate has also been obtained from natural sources such as lakes, sea, wells and solid salt deposits [8].

Leblanc process involving interaction of sodium chloride with sulphuric acid is currently being used for the production of sodium sulphate. The main constraint in this process is the high cost of sulphuric acid which prevents its use for the production of a relatively low-price product such as sodium sulphate.

The present work reports a process in which costly chemicals like sulphuric acid have been replaced by gypsum and with the use of ion exchange resin, sodium sulphate of technical grade has been obtained. The process consists of

picking up the sulphate radical on an ion exchange resin and leaching it out as sodium sulphate with sodium chloride.

### MATERIALS AND METHOD

Gypsum from the Kohat fields and common salt of the Khewra salt mines were used in the present studies. Amberlite IR 120 cation exchange resin with polystyrene sulphonic acid base and exchange capacity of 350 g CaSO<sub>4</sub>/cu.ft. and mesh size 14–52 was employed.

For the exchange reaction, columns were made from two pipes of PVC with 20 cm and 150 cm length closed at both ends with PVC plates and each having an inlet and outlet for the entry and exit of the solution.

For concentration and crystallisation of the sulphate, a stainless steel tray type evaporation pan of 150 cm x 100 cm x 15 cm dimension was used.

Stirring of gypsum powder with ion exchange resin was achieved by using a locally improvised stirrer with 400 rpm.

Sodium sulphate in the effluent was estimated by the standard barium chloride method [9] and contamination of calcium was detected by ammonium oxalate method [10].

*Solar Evaporator.* Solar evaporator with dome shaped top made of plastic sheet supported on steel ribs to allow sunlight from all directions and concrete lined base was used for solar evaporation. The dome was placed in such a way that it was raised seven centimetres above the ground level to allow escape of vapour while maintaining temperature of 70–80°.

*Recovery of Sodium Chloride and Calcium Chloride.* The exhausted salt solution is evaporated to the saturation level of sodium chloride whereby crystals of sodium chloride appear. These are recovered by centrifugation in a



basket centrifugal machine and calcium chloride solution is concentrated to get the required grade.

#### Transformation of Gypsum into Sodium Sulphate.

Gypsum was converted into sodium sulphate by ion exchange method applying two different models of operation.

1. *Agitation Method:* 100 litres of permutit cation exchange resin is agitated in a 200 litres vessel with 40 litres of 15 % solution of sodium chloride for 10–15 min. The salt solution is then drained by means of a bottom tap and the resin is washed by stirring with water till free from salt. In a separate vessel 1 kg of pulverised gypsum of 200, 300 and 400 mesh size is mixed with 50 litres of water respectively and stirred. The resultant turbid suspension of gypsum is then poured into the vessel containing the resin and the mass is stirred gently for 5, 10, 15, 20, 25 and 30 min to allow absorption of the calcium sulphate of gypsum on to the resin. The end point reaches when the turbidity due to insoluble gypsum particles disappears and the concentration of the resulting sodium sulphate solution comes to about 2 % level which is the saturation point. The resultant solution of sodium sulphate is subjected to primary evaporation in solar tank followed by final evaporation in steel pans to obtain crystals of Glauber's salt which are then dried further to obtain anhydrous sodium sulphate. The conversion was 90 % on the basis of gypsum.

2. *Column Method:* In this method instead of ground gypsum,  $\frac{1}{4}$ " to  $\frac{1}{2}$ " pieces are packed in a column. 50 litres of water are then passed through this column such that gypsum saturated solution is obtained. It is led to another column containing 100 litres of activated resin. The out-flowing solution of sodium sulphate from this column is again fed to the gypsum column and the circulation continued till the concentration of sodium sulphate reaches about 2 % level. The two columns are interconnected in such a way that water enters the gypsum column at the base and leaves the column from the top entering the resin column from the base and leaving this column from the top. The solution is concentrated as described in Method 1 and the yield obtained was approximately 90 % as in Method 2.

### RESULTS AND DISCUSSION

Fig. 1 shows the effect of particle size on the rate of formation of sodium sulphate from gypsum in the presence of resins during agitation process. It is apparent that in the case of 400 mesh size suspension only seven minutes are required for reaching the maximum 2 % level of sodium sulphate whereas in the case of 300 and 200 mesh, the approximate time required was 13 and 28 min respectively. The rate of exchange of calcium is maximum in the suspension made with 400 mesh gypsum. It seems that due to larger surface area offered by the fine particle size of gypsum an increased solubility of this sparingly soluble electrolyte could be achieved.

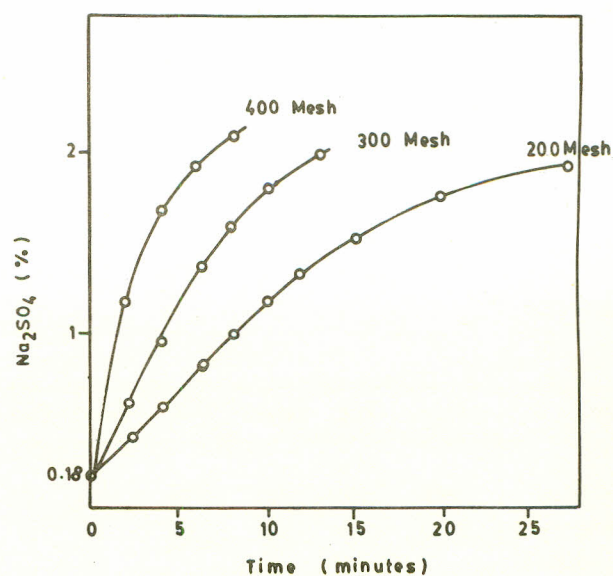


Fig. 1. Effect of particle size on the rate of formation of sodium sulphate

Table 1 shows that the concentration of sodium sulphate in the effluents of the column process increase with an increase in the number of circulations through the column of gypsum and resin, reaching from the initial value of 0.2 % after first circulation to the final value of 2 % sodium sulphate after the tenth circulation. This increase can be attributed to the continuous removal of the soluble (0.20 %) calcium sulphate from the circulatory fluid by the resin which allows more dissolution of gypsum which is subsequently converted into sodium sulphate. The resulting increase concentration of sodium sulphate in the fluid plays

Table 1. Concentration of sodium sulphate in effluents of resins column after each circulation (column method).

No. of circulations	% Sodium sulphate	Column ions
1	0.20	—
2	0.38	—
3	0.60	—
4	0.80	—
5	1.00	—
6	1.20	—
7	1.40	—
8	1.55	—
9	1.85	—
10	2.00	—
11	2.10	+
12	2.10	+
13	2.20	++
14	2.40	++++



Table 2. Seasonal variation of the yield of sodium sulphate from the solar tank with 25 litres capacity.

Months	Jan.	Feb.	March	April	May	June
Yield (g)	150	150	250	250	500	500
Litres evaporated.	7.5	7.5	12	12	25	25

Months	July	Aug.	Sept.	Oct.	Nov.	Dec.
Yield (g)	450	100	200	200	200	150
Litres evaporated.	22.5	5	10	10	10	7.5

an important role in solubilising more of gypsum by salt effect. Cameron *et al.* [11] during studies on the solubility of gypsum found that 2.3 % sodium sulphate enhanced the solubility of gypsum from 0.18 to 1.65 %.

In our experimental studies it was observed, that absorption of calcium ions on the resin is suppressed beyond the value of 2 % sodium sulphate. This may be due to the saturation of resin with calcium ions or to an increase in the concentration of sodium ions which reverses the absorption of calcium ions because of stronger affinity of sodium ions for the resin. Although very simple and continuous this method yields solution with maximum concentration of sodium sulphate. The solution is however, very pure if contamination with calcium ions is monitored continuously. To obtain solid product from such dilute solution, the concentration tends to be expensive due to high cost of fuel. Solar evaporation of these solutions was, therefore, attempted. The drying rate of such a solution in the Lahore region during the year has been shown in Table 2. It has

been noted that with a charge of 2 litres/sq. ft. the solar tank could cause the evaporation of 25 litres of the solution per day yielding 500 g solid anhydrous sodium sulphate during the month of May and June.

The ion exchange method employed in the present work can be made more feasible by either finding resin of high exchange equivalents for calcium or by constructing solar tank in areas selected for such a project. Under the conditions employed, solar drying method could make this process feasible.

The present method is unique in the sense that it does not involve any chemical processing, using chemicals other than sodium chloride. The ion exchange resin can be recovered without any extra cost by treatment with sodium chloride.

#### REFERENCES

1. H. Bauer, German Pat. D.R.P. 52636, (1889).
2. S.N. Stavrov and S.D. Shargosodskii, *Roboty po Knium. Chlenov Krymsk. Otd. Khium Obshenestra im. D.I. Mendeleera (Scienferofols Krymizdat) 97-101* (1961).
3. Joseph N. Maurad, *Brit. 722, 069*, Jan. 19, 1955.
4. Silvia Tilenschi, Stefan Lupan, Iacob Samoil and Ion Strugaru. *Ram. 47,825 (Cl. COID, b) 1967*.
5. Georgeta Budici, Klisaluta Serbam, and Valeria Ionescu. *Rev. Chem. (Bucharest) 10,559-62* (1959).
6. R.C. Trumbul, W. Hardiek and E.G. Kawfird *Bull. Inst. Mining Met. 505, 1-25* (1948).
7. A. Hirsch. *U.S.P. 2, 392, 669* (1946).
8. Exploitation of great salt lake, *Chem. Eng. 75, No. 13, 106-110* (1968).
9. A.I. Vogel, *Quantitative Inorganic Analysis*, 3rd edition, p. 462.
10. A.I. Vogel, *Quantitative Inorganic Analysis*, 3rd edition p. 473.
11. F.K. Cameron and J.F. Beazeale, *J. Phy. Chem., 7, 335* (1903).